

In Situ Chemical Oxidation (ISCO): Current Advancement

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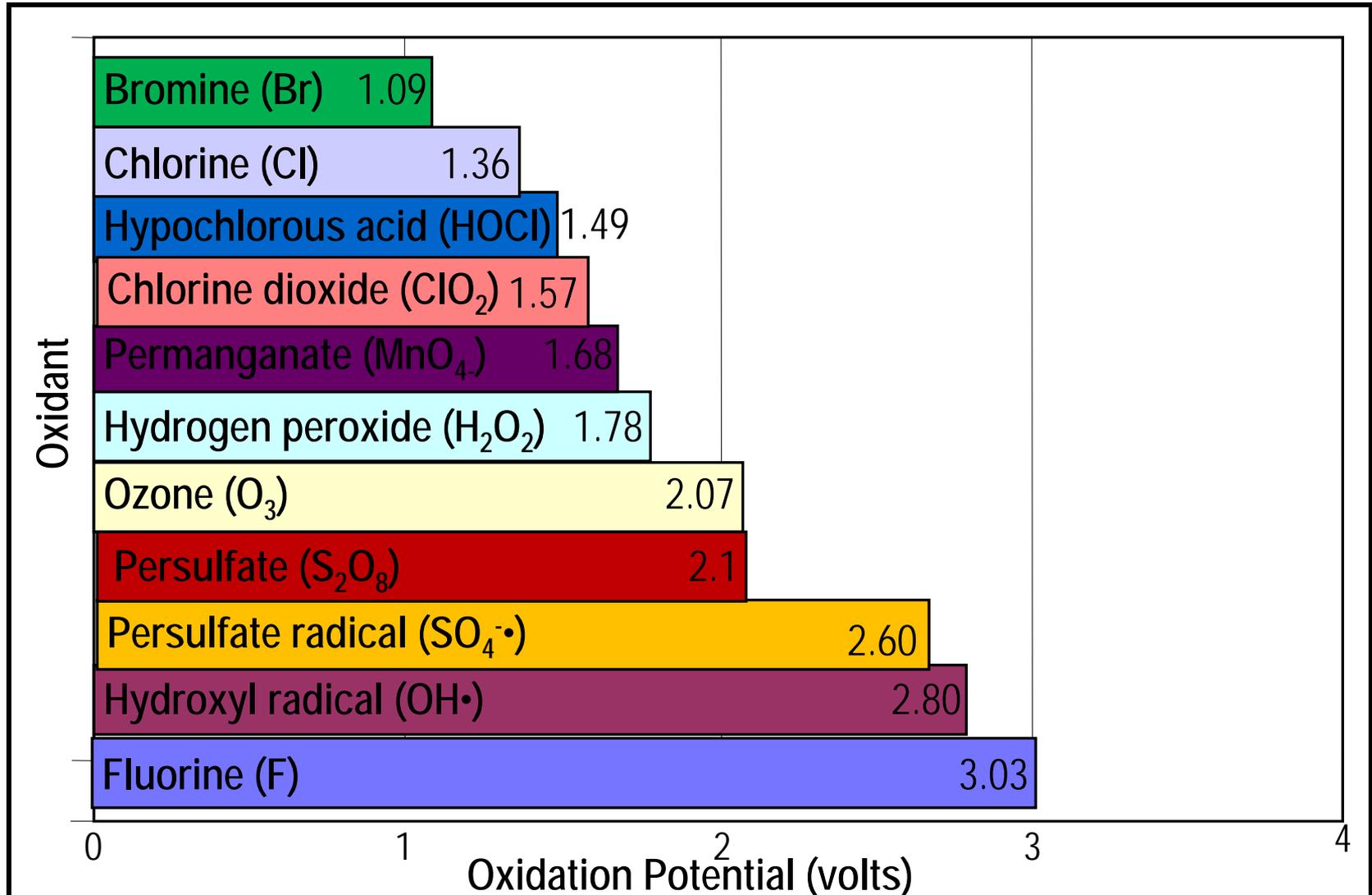
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Principles of Common Oxidation Processes

An oxidant is a chemical that has a tendency to accept electrons from other chemicals (preferably target contaminants in groundwater and soil)

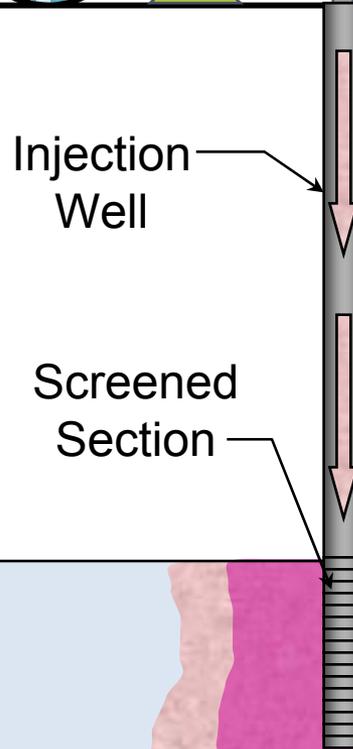
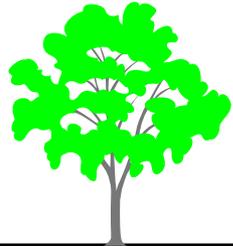
- The target contaminant is oxidized (loses electrons) and is transformed to a non-toxic or less-toxic product
- Oxidation potential is a measure of the oxidative power of an oxidant. The higher the oxidation potential (volts), the greater the oxidative power.

Oxidation Potential of Select Oxidants



ISCO Conceptual Injection Process

Reagent is injected and occupies set volume



MnO_4
 H_2O_2
 S_2O_8



Contaminated Aquifer

Spread of Reagent

Residual DNAPL



Groundwater Flow Direction →

ISCO Definitions

- Can be used to treat dense, nonaqueous-phase liquid (DNAPLs) as well as dissolved-phase contaminants
- Does not rely on biological processes
- May not require aboveground treatment, as with pump and treat (P&T) systems, thermal heating, and surfactant flushing

Advantages and Limitations

- Advantages

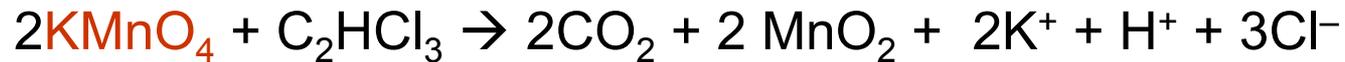
- Can destroy contaminants *in situ* (unlike thermal or surfactant flushing technologies)
- Reagents relatively inexpensive (e.g., KMnO_4 at \$1 to \$1.50/lb)
- Is potentially effective with many different types of organic contaminants in sorbed and DNAPL states
- Is cost-effective for contaminant source zones or "hot spots"

- Limitations

- Has some handling hazard (e.g., hydrogen peroxide)
- As with any in-situ technology, reagent delivery to the target regions may be challenging
- Strong oxidants may oxidize other (naturally occurring) reduced species in the subsurface
- An injection permit may be required
- May not be cost-effective for treating very dispersed, dilute contamination (i.e., dispersed contaminant plume)

Common Oxidant Chemistries

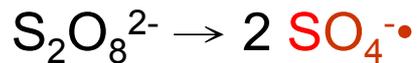
- Permanganate oxidation



- Fenton's Reagent



- Persulfate



Permanganate – Target Contaminants

- Permanganate has been shown to oxidize:
 - Chloroethenes (e.g., TCE)
 - PAHs
 - Chlorinated pesticides (e.g., aldrin and dieldrin)
 - High explosives
 - Some chlorophenols
- Permanganate is ineffective with:
 - Chlorinated alkanes (e.g., TCA, dichloroethane)
 - Aromatic hydrocarbons (e.g., benzene and chlorobenzene)
- MTBE – is oxidized to TBA
 - Functional group is oxidized, but not the parent structure

Permanganate Reagents

- Sodium permanganate
 - Supplied as dark purple liquid (40% min. conc.)
 - No concerns with dust
 - More expensive than KMnO_4
- Potassium permanganate
 - Supplied as crystalline solids
 - Mixed onsite
 - Concerns with dust
 - Derived from mined potassium ores; hence contains small amounts of impurities, such as metals, ^{40}K , etc.



KMnO_4 Solution

Factors Affecting Permanganate Application

- Soil oxidation demand (SOD) often exceeds the oxidant demand of the COC, sometimes by 2 or 3 orders of magnitude
 - **Reduced solid species (e.g., sulfides, ferrous iron minerals, etc.)**
 - **Natural organic matter**
 - **Aqueous species (dissolved iron, etc.)**
- **Near potential receptor (purple water)**

Advantages and Limitations: Fenton's Reagent

- **Advantages**

- Hydroxyl free radical is much more reactive than permanganate and can therefore oxidize many more COCs
- Reactions that generate multiple free radicals destroy nearly all organic contaminants
- Ability to treat strongly sorbed and DNAPL contaminants
- Chemicals involved do not appear to contain trace impurities of concern
- Color is not a concern
- No significant generation of solids that could clog the aquifer

- **Limitations**

- Peroxide and hydroxyl free radicals are extremely short-lived and this could limit distribution (reaction rate is diffusion controlled). Other reactive species generated are more long-lived.
- Safety issues with H_2O_2
 - ✓ **Chemical fires and explosions**
 - ✓ **Chemical burns**
- ✓ Reaction is highly exothermic and higher peroxide concentrations can cause steaming and volatilization of COCs

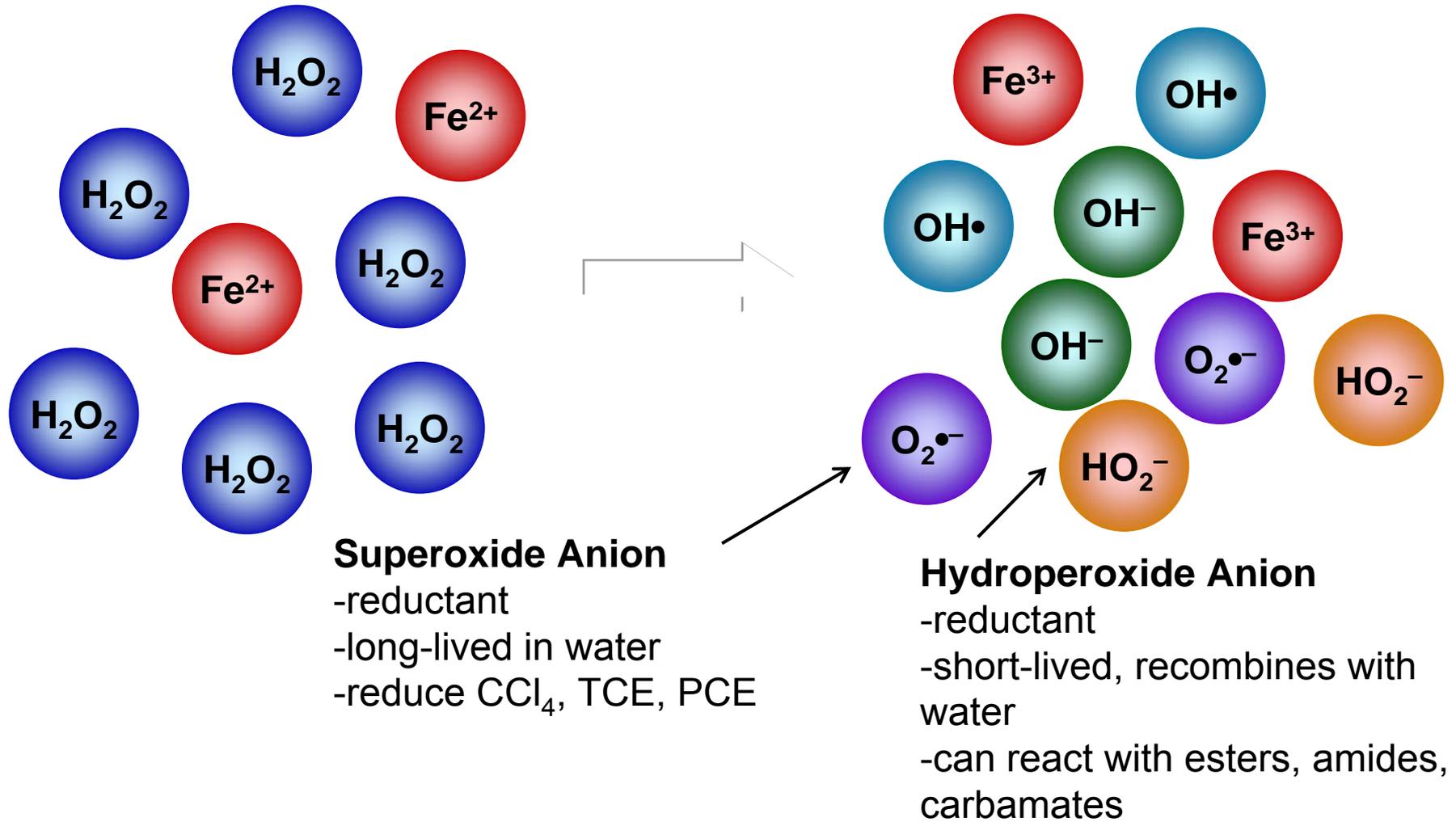
Compounds Not Reactive with Hydroxyl Radicals (OH•)

- Halogenated Alkanes
 - Carbon tetrachloride
 - Hexachloroethane
 - Chloroform

Modified Fenton's Reagent Applications

- Use of relatively high hydrogen peroxide concentrations
(typically 2%-12% H₂O₂)
- A range of different materials can catalyze the generation of free hydroxyl and other reactive radicals
 - Soluble Iron (II): Most common so far, with the addition of FeSO₄
 - Iron (III)
 - Naturally occurring minerals
 - Iron chelates

Modified Fenton's Reagent: Formation of Other Reactive Species



Catalysis by Iron Chelates

- Iron-EDTA (Ethylenediaminetetraacetic Acid)
- Iron-NTA (Nitrilotriacetic Acid)
- Iron-Citrate

Advantage:

- Promote Fenton's reactions at neutral pH

Disadvantages:

- High potential for metals mobility
- Chelate is oxidized

Catalysis by Iron Minerals

- Natural soil minerals can catalyze the reaction and form reactive radicals
- At many sites, there may not be a need to add ferrous compounds
- pH 3 to 4 required (acid addition)
- pH rebounds after treatment
- Releases carbonates as CO_2
- Provides highest degree of H_2O_2 stability
- Addition of an iron catalyst not required

Factors Affecting Fenton's Reagent Application – Presence of COCs as DNAPL

- Evidence from the field has indicated DNAPL destruction by Fenton's reagent
- DNAPL destruction by Fenton's reagent has been documented through laboratory research and occurs more rapidly than any other treatment process (up to 50x the rate of natural dissolution)
- DNAPL destruction most likely does not involve hydroxyl radicals, but is likely superoxide
- Even when dissolved COC concentrations do not show a significant decrease, considerable DNAPL mass may have been oxidized
 - Exothermic reaction may cause higher desorption
 - DNAPL destruction may cause improved advective flow and higher dissolved concentrations

Peroxide Distribution and Dosing

- Peroxide instability limits distribution
 - Primary catalysts for the unproductive decomposition of hydrogen peroxide in subsurface are manganese oxides
- Formation of large volume of vapor

Implication: Treatability tests should be conducted to monitor peroxide decomposition rates, and therefore, the well spacing, need for vapor recovery, etc.



Gas in Monitoring Well during Fenton's Application

Peroxide Distribution and Dosing (Cont.)

- Optimum hydrogen peroxide concentrations are usually 0.5%-12% and are highly site specific
 - Lower concentrations (0.5%-1%) are most effective when contaminants are not sorbed and DNAPLS are not present
 - Higher concentrations (2%-12%) are usually required to treat sorbed and DNAPL contaminants
 - Concentrations >12% are problematic because of highly exothermic reactions and rapid decomposition of hydrogen peroxide

Advantages and Limitations of Persulfate

- Advantages

- Sulfate free radical is much more reactive than permanganate and can therefore oxidize many more COCs
- Less oxidant demand than permanganate
- More stable than the hydroxyl free radical
- Ability to treat strongly adsorbed and DNAPL contaminants
- Color is not a concern
- Minimal safety issues (primarily dust)

- Limitations

- Requires on site mixing
- As with all oxidants, application can mobilize metals
- Newer, less understood than other reagents
- Forms sulfuric acid, can lower aquifer pH
- May degrade soft metals (copper, brass)
- Requires an activation agent for best results

Available Forms of Persulfate

- Ammonium persulfate
- Potassium persulfate
 - Limited solubility in water (6%)
- Sodium persulfate
 - Most commonly used
 - Supplied as crystalline yellow solid, mixed on site
 - Relatively high solubility in water (40%)

Persulfate Activation Methods

- Iron
 - Requires low pH or chelating agent (similar to Fenton's)
 - Efficiency decays with time and distance from injection
 - Optimum loading of 100 to 250 mg/L
 - May not need to add at some sites
- Heat (steam or resistive heating)
- Alkaline (pH >10)
 - sodium hydroxide
 - Shown to oxidize chloromethane, chloroform, and TCA
- Hydrogen peroxide

Reagent Application Methods

- Direct injection - The reagents are injected directly into the subsurface in a specified volume of water from an external source, displacing groundwater corresponding to the volume of reagent injected
- Pull-Push: A set volume of groundwater is extracted, amended with reagents above ground and then reinjected into the subsurface through the same well
- Recirculation: In a closed system, groundwater is extracted from a set of extraction wells, amended with the reagents and then reinjected into a different series of injection wells.

Multiple injections may be required!!!

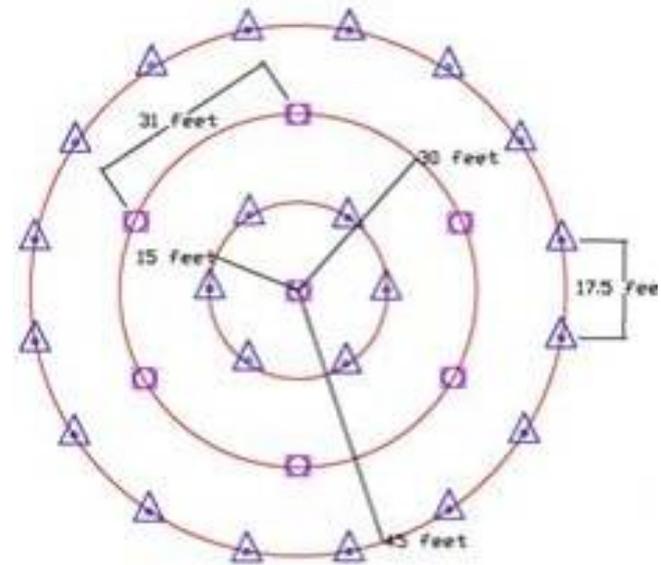
Oxidant Application - Direct Injection

- Injection Only (currently more practiced, viewed as "easy")
- Injection wells have to be arranged in a way that makes use of natural gradient to distribute the oxidant
- Or, use multiple temporary injection points to inject the oxidant in several locations and depths in the target treatment zone
- Higher injection pressures may be required in tighter soils (possibility of spreading the COCs)
- Mn (discoloration) and trace metals could migrate downgradient

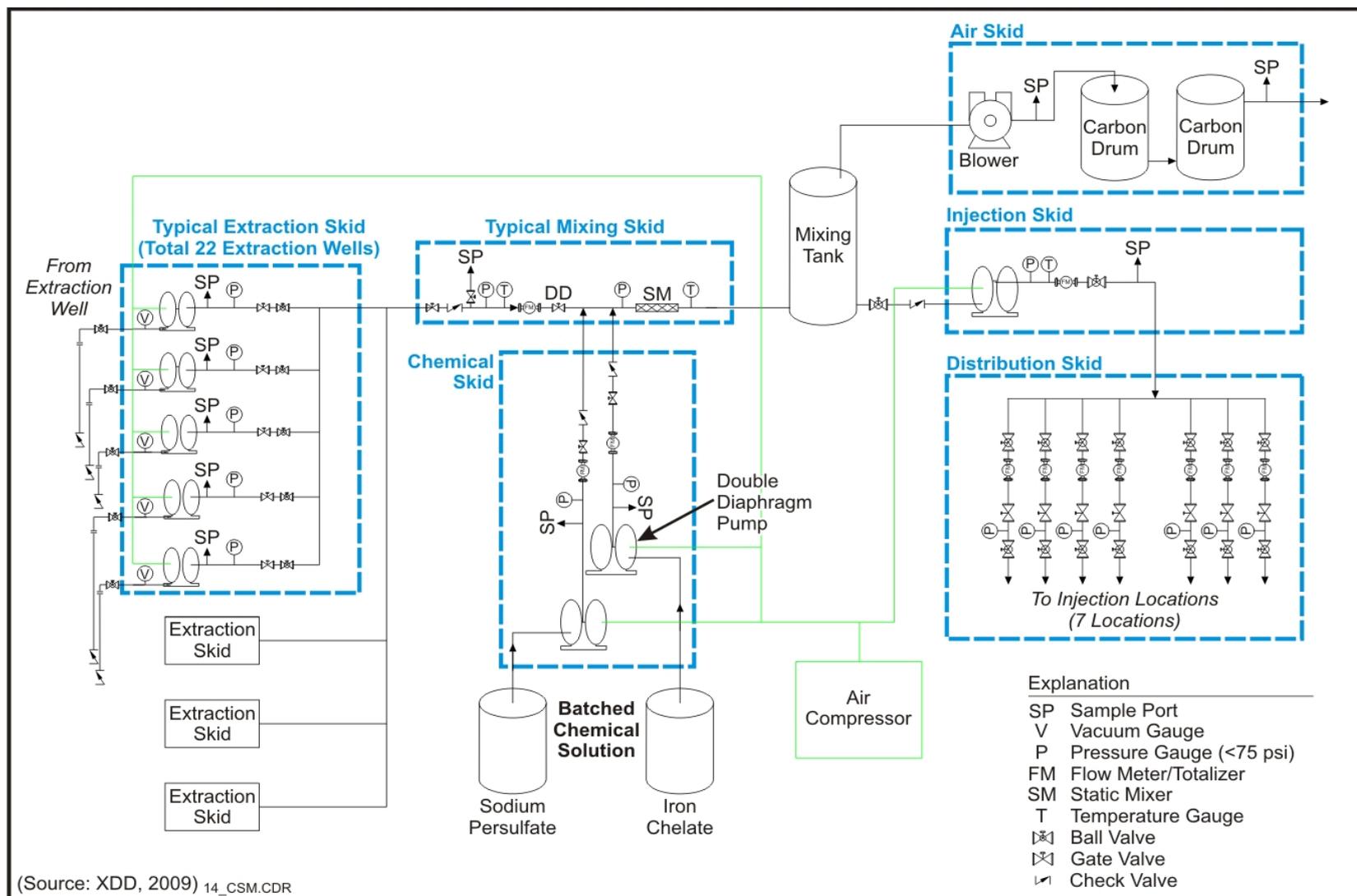


Oxidant Application - Recirculation

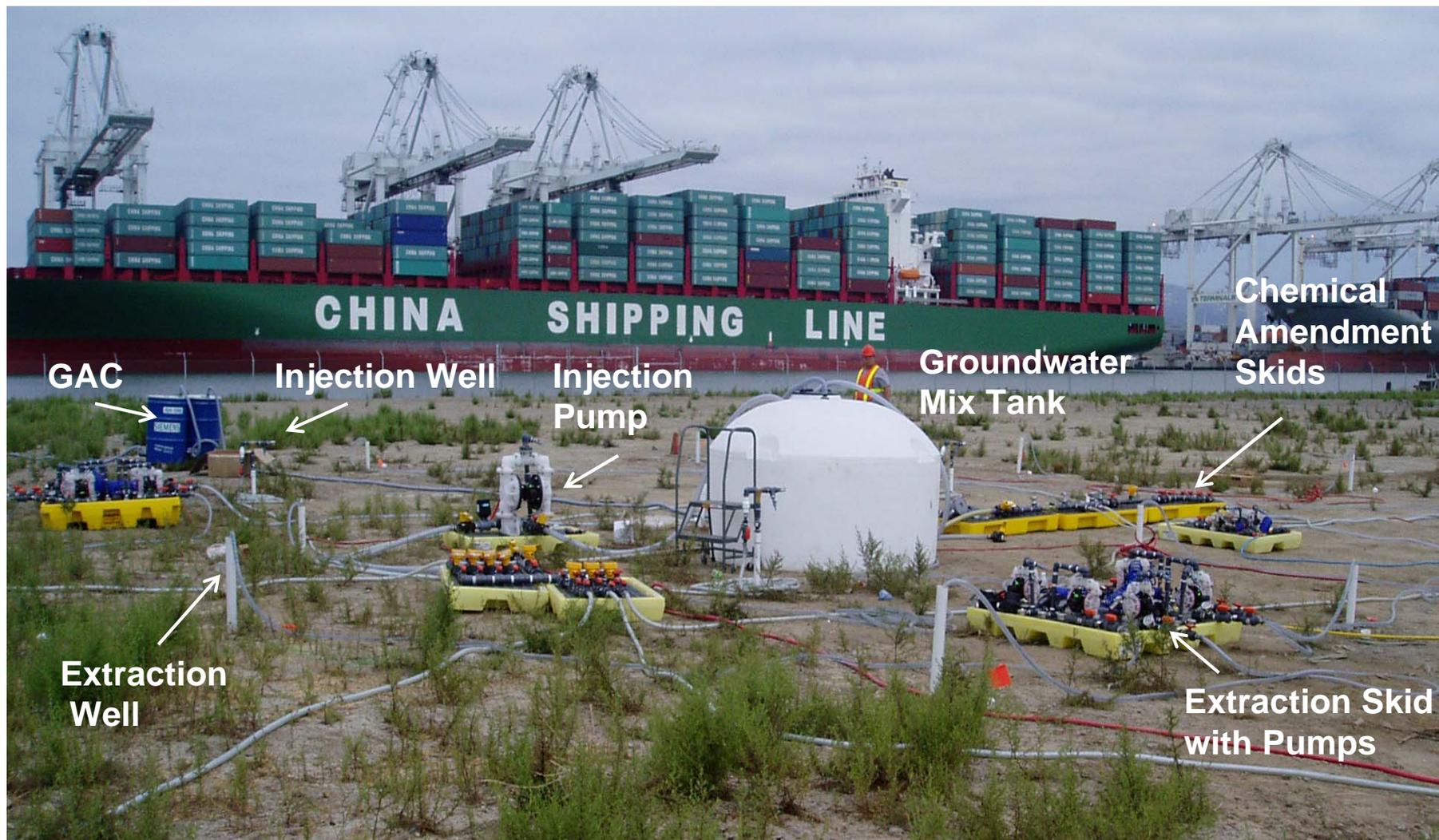
- Better hydraulic control – better distribution of oxidant, less chance of COC migration
- Reinjection may need to meet stricter guidelines
- More elaborate aboveground equipment required
- Typically lower oxidant dosing
- Minimizes potential for surfacing



PID Drawing ISCO System



Example System Layout



Health and Safety Considerations

- Most safety concerns associated with application of hydrogen peroxide
- Proper personal protective equipment, including face shields, glasses, Tyvek® aprons, reinforced-toed boots, hard hats, are worn while working in the work zone
- Chemical oxidants must be stored within secondary containment pads
- Carefully monitor temperatures and pressures
- Injections discontinued if surfacing of reagents (“daylighting”) occurs
- Seals equipped with pressure relief valves installed on all injection points and monitoring wells to control release of fluids from wells



Process Monitoring

- Performed during application
- Injection pressures, flowrates, and temperatures
- Groundwater quality parameters (very useful)
- Reagent levels in monitoring wells and extracted and injected water using real time analytical techniques
- Aboveground destruction of ethenes (in the case of recirculation)

Target Area	Volume Extracted ^(a)		Volume Injected ^(b,c)	Sodium Persulfate			Activator Solution ^(b,e)
	Volume (gal)	% Pore Volume ^(f) (gal)		Volume solution ^(d) (gal)	Mass (lbs)	Conc. (g/L)	
1	60,400	60	63,700	2,600	6,600	12	727
2	34,600	46	38,500	3,060	6,600	21	839
3	41,800	41	45,000	2,440	6,600	18	782
Totals	136,800		147,200	8,100	19,800		2,348

Performance Monitoring

- Performed after concluding reagent injections
- May be performed quarterly or semi-annually
- VOCs and metals
- Groundwater quality measurements (pH, ORP, DO, temperature, and conductivity)
 - Is aquifer geochemistry returning to baseline conditions?
- Groundwater levels

